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(REV. 1094)

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET
NUMBER
C1043/7023

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/529873

INTERNATIONAL APPLICATION NO.
PCT/GB98/03154

INTERNATIONAL FILING DATE
21 October 1998 (21.10.98)

PRIORITY DATE CLAIMED
21 October 1997 (21.10.97)

TITLE OF INVENTION
POLYMERIC MATERIALS FOR ELECTROLUMINESCENT DEVICES

APPLICANT(S) FOR DO/EO/US

HOLMES, Andrew Bruce; CHUAH, Beng Sim; CACIALLI, Franco; MORATTI, Steven Carl

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

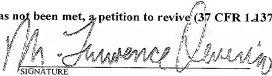
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(C)(5)).

Items 11. To 16. Below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment (with amended claims).
 - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification (submitted as a first Preliminary Amendment).
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
 - Mailed via Express Mailing Label No. EM529190389US
 - Published Application with Search Report
 - Post Card

Mailing Date: April 20, 2000
Express Mail Label No. EM529190389US

422 Rec'd PCT/PTO 2 0 APR 2000

U.S. APPLICATION NO. (if known, see 37 CFR 1.51) 09/529873		INTERNATIONAL APPLICATION PCT/GB98/03154		ATTORNEY'S DOCKET NUMBER C1043/7023	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS <small>PTO USE ONLY</small>	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):					
Search Report has been prepared by the EPO or JPO				\$840.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482)				\$670.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))				\$760.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$970.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)				\$96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than ~ 20 X 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	26 - 20 =	6	X \$18.00	\$ 108.00	
Independent Claims	2 - 3 =	0	X \$78.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+\$260.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 948.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$ 948.00	
Processing fee of \$130.00 for furnishing the English translation later than ~ 20 ~ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 948.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate coversheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$ 948.00	
				Amount to be: refunded \$	
				charged \$	
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>948.00</u> to cover the above fees is enclosed.					
b. Please charge by Deposit Account No. _____ In the amount of \$ _____ To cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23/2825. A duplicate of this sheet is enclosed.					
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <div style="text-align: right; margin-top: 10px;">  SIGNATURE </div>					
SEND ALL CORRESPONDENCE TO					
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> Therese A. Hendricks WOLF, GREENFIELD & SACKS, P.C. 600 Atlantic Avenue Boston, Massachusetts 02210 </div> <div style="width: 45%; text-align: right;"> M. Lawrence Oliverio NAME 30,915 REGISTRATION NO </div> </div>					

ATTORNEY'S DOCKET NO: C1043/7023

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Holmes et al.
Serial No: --
Filed: Herewith
For: POLYMERIC MATERIALS FOR ELECTROLUMINESCENT
DEVICES

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Please amend the above application as follows to conform the specification with U.S. practice.

In The Specification

- ◆ On page 1, before the first paragraph, please add the subheading -- Field of the Invention --
- ◆ On page 1, before the second paragraph, please add the subheading -- Background of the Invention --
- ◆ On page 2, line 7, please add the subheading -- Summary of the Invention --
- ◆ On page 3, line 21, please add the subheading -- Brief Description of the Drawings --;
- ◆ On page 4, line 12, please add the subheading -- Detailed Description --

In The Claims

Please amend the claims as follows:

- ◆ In claim 4 delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 5, delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 6, delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 7, delete "any preceding claim" and substitute -- claim 1 --

- ◆ In claim 8, delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 9, delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 10, delete "any preceding claim, which" and substitute -- claim 1, wherein the poly(arylene vinylene) --
- ◆ In claim 12, line 2, delete "any of claims 1-7" and substitute -- claim 1 --
- ◆ In claim 14, delete "any preceding claim" and substitute -- claim 1 --
- ◆ In claim 16, delete "or 15"
- ◆ In claim 17, delete "any of claims 1-13" and substitute -- claim 1 --
- ◆ In claim 18, delete "which is" and substitute -- further comprising --
- ◆ In claim 19, delete "or claim 18"
- ◆ In claim 19, delete "which is" and substitute -- further comprising --
- ◆ In claim 20, delete "any of claims 17-19" and substitute -- claim 17 --
- ◆ In claim 21, line 1, delete "as defined in any of claims 17-20"
- ◆ In claim 21, line 2, delete "any of claims 1-13" and substitute -- claim 1 --
- ◆ In claim 23, delete "or claim 22"
- ◆ In claim 24, delete "any of claims 21-23" and substitute -- claim 21 --

Please cancel claims 25-29.

Please add the following new claims 30 and 31:

-- 30. A light emitting diode having a coating of a compound according to claim 1.

31. An electric, electronic, optical or optoelectronic component or device having a coating of a poly(arylene vinylene) compound comprising an arylene unit having adjacent substituents which produces blue-shifted electroluminescence or photoluminescence. --

Date: April 19, 2000
Docket No. C1043/7023

POLYMERIC MATERIALS FOR ELECTROLUMINESCENT DEVICES

The present invention is directed to polymers for use in electric, electronic, optical and optoelectronic devices, e.g. polymer-based light-emitting devices, such as light emitting diodes (LEDs). In particular, the present invention concerns poly(1,4-arylene vinylene)s which have improved photoluminescence and/or electroluminescence efficiencies.

The potentially high photoluminescent quantum yield in organic semiconductors has made light emission through charge injection under an applied field (electroluminescence) a reality. This has thus resulted in the use of organic materials for LEDs, with the use of polymers having an advantage over smaller organic compounds in improving structural stability and processibility of the organic layers.

The first polymer-based LEDs consisted of an emissive layer of poly(1,4-phenylene vinylene) (PPV) sandwiched between indium tin oxide (ITO) as the hole injection electrode and aluminium or calcium as the electron-injecting electrode (Burroughes *et al.*, *Nature*, 1990, 347, 539). This has been followed in other polymers for LED applications, with emphasis on the tuning of the emission colour by controlling the substitution pattern and the effective conjugation length in the polymer.

The route used for the synthesis of PPVs for LEDs has been predominantly the Wessling¹² sulphonium salt precursor route (U.S. Pat. 3,401,152/1968 Wessling *et al.*) while another important method of Gilch (Gilch *et al.*, *J. Poly. Sci.* 1-A, 1966, 4, 1337), involved dehydrohalogenation of bis(halomethyl) benzene monomers with excess potassium *t*-butoxide to directly obtain the conjugated polymer. This protocol has been applied to the red emissive poly(2,5-dialkoxy-1,4-phenylene vinylene)s which have a typical absolute PL efficiency of ca. 15-20%. Most commonly the preparation has referred to poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (Wudl, U.S. Pat. 5,189,136/1990). A modification of this route by Swatos and Gordon, based on the chloro-precursor route, used one equivalent of base to form the chloro-substituted soluble precursor polymer, which was then thermally converted to form the fully conjugated polymer [Swatos and Gordon, *Polym. Prepr.*, 1990, 31 (1), 505]. This route has since

been used by various groups to make alkyl-, aryl- and alkoxy-substituted PPVs (Hsieh *et al.*, *Adv. Mater.*, 1995, 7, 36; *Polym. Adv. Tech.*, 1997, 8, 392; U.S. pat. 5,558,904; Sarnecki *et al.*, *Synth. Met.*, 1995, 69, 545).

There is still a need to provide photoluminescent and electroluminescent polymers, which are easily manufactured and are processible. There is also still a need for polymers having improved photoluminescence and electroluminescence efficiencies.

It is an object of the present invention to solve the above problems. Accordingly, the present invention provides a conjugated poly(1,4-arylene vinylene) compound comprising an arylene unit having adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

The present invention also provides use of a poly(arylene vinylene) compound comprising an arylene unit having adjacent substituents, in an electric, electronic, optical or optoelectronic component or device for producing blue-shifted electroluminescence or photoluminescence in said device.

The substituents may affect the electronic structure of the compound by exerting a steric or electronic effect, such as a twisting of the polymer backbone to accommodate their steric bulk, which twisting leads to a reduction in the conjugation of the compound. The reduction in conjugation in turn leads to a blue-shift in luminescence. Additionally, the substituents may possess one or more lone pairs of electrons which may interfere with the conjugation in the polymer to cause the blue-shift in luminescence.

The blue-shift is a blue-shift as compared with a hypothetical compound, this being the same polymer in which the orientation of the substituents (whether resulting from their steric bulk or some electronic effect) has no effect on the electronic structure of the compound. Thus, for example, the blue-shift may be a blue-shift resulting from a reduction in conjugation caused by

twisting the backbone of the polymer to the degree required to accommodate the steric bulk of the substituents.

The present invention describes the surprising discovery of efficient blue-shifted emission from poly-1,4-(arylene vinylene)s having adjacent substituents, preferably 2,3-disubstituted PPV-based materials and their use in LEDs. This invention explores unconventional substitution patterns, e.g. in the case of poly(phenylene vinylenes) (PPVs) at the 2,3-positions on the phenyl ring as opposed to the standard 2,5-disubstituted PPVs and thus provides a means of tuning the colour of emission. In addition, the present invention provides a luminescent polymer that is both soluble and directly obtainable, preferably by the Gilch route. The invention refers to the synthesis of improved materials and their application in organic LEDs.

The present invention also provides materials-based light-emitting devices, such as light emitting diodes (LEDs), in which the use of a layer of emissive polymer enables efficient devices to be constructed using aluminium or calcium cathodes. The polymer is a poly(1,4-arylene vinylene) having adjacent aryl substituents, preferably a poly(1,4-phenylene vinylene) (PPV) derivative, having substituents on the 2,3-positions of the phenylene ring. This substitution pattern produces a blue-shifted emission and high PL and EL device efficiencies. The polymerisation route is simple, the polymer is soluble, and displays good film forming properties with high photoluminescence in the solid state.

The invention will now be described in further detail by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows the X-ray crystal structure of oligomer 9;

Figure 2 shows absorption and PL spectra of films of oligomer 9;

Figure 3 shows absorption spectra of PDB PPV 1 compared with a PPV film;

Figure 4 shows PL spectra of PDB PPV 1 compared with PPV film and EL spectra of a bilayer device (configuration ITO/PPV/PDB-PPV 1/Ca)

Figure 5 shows a plot of current density vs. applied voltage for a bilayer device (configuration ITO/PPV/PDB-PPV/Ca)

Figure 6 shows absorption and photoluminescence spectra of films of copolymers 12 and 13;

Figure 7 shows I-V-L plots for single layer device ITO/15C5-DB PPV 12/Al;

Figure 8 shows I-V-L plots for single layer device ITO/15C5-DMOS PPV 13/Al;

Figure 9 shows I-V-L plots for double layer device ITO/PPV/15C5-DMOS PPV 13/Al, at drive voltages *ca.* 14V, EL quantum efficiency up to 2.0%;

Figure 10 shows a CV plot of 15C5-DB PPV copolymer 12; and

Figure 11 shows a CV plot of 15C5-DMOS PPV copolymer 13.

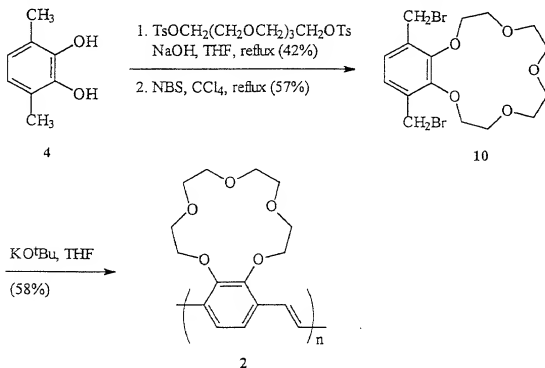
The electroluminescent (EL) devices according to the present invention are injection-type diodes in which at least one active layer (EL layer) and one or more charge transport layers (if desired) are sandwiched between two different conducting layers (electrodes). One electrode is a hole-injecting translucent or transparent electrode while the other is an electron-injecting electrode. The electrodes are electrically connected to each other and to a source of current to create a complete circuit. Improved efficiencies may be obtained using bilayer devices with PPV or hole transporting layers e.g. poly(vinyl carbazole) (PVK).

This invention refers in one specific embodiment to the polymer, poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] 1 which can be prepared using the dehydrohalogenation method with base (potassium *tert*-butoxide). The resultant polymer has high molecular weight and its alkyl chains enable solubility in organic solvents such as chloroform and tetrachloroethane. Surprisingly, the solid film fluoresces with high efficiency (absolute PL efficiency 40%) in the

In a further embodiment, the invention extends to the fluorescent oligomer **9** which has been synthesised using the Wadsworth-Emmons reaction of a dialkoxybenzyl bisphosphonate **8** and dialkoxy-benzaldehyde **7**. Evidence for the origin of the blue-shifted emission and possible high fluorescence efficiency comes from the single crystal X-ray study of **9** which shows that the aromatic rings are twisted in a notable manner, thus resulting in the disruption of the effective conjugation length of the polymer backbone. The localisation of the conjugation could also be due to the cisoid-like disposition of the styryl substituents in **9** (see Figure 1).

Scheme 1: Structure of the poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) **1** and the crown ether analogue **2**

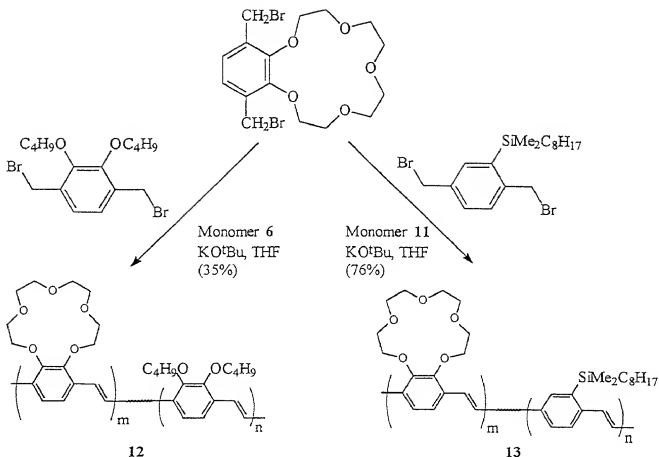
The crown ether analogue **2** is also fluorescent. It can be prepared as shown in Scheme 2 below:



Scheme 2: Preparation of 15C5 crown ether **2**

As the polymer **2** is also luminescent it can be used advantageously in light emitting electrochemical devices and other devices where chelation of various metal ions, preferably lithium, can lead to ionically doped materials fabricated out of a homogeneous phase rather than from a blend of more than one polymer which may phase-separate. Such doping can lead to reduced barriers for charge injection into the emissive layers. Statistical copolymers derived from dehydrohalogenation condensation polymerisation of the building block **10** with either the DMOS precursor **11** or the dibutoxy precursor **6** afford efficient devices (Scheme 3). The ratio of m:n may range from 10:1 to 1:10, preferably ca. 1:1.

7



Scheme 3: Statistical copolymers 12 and 13

Two layer devices were fabricated using 1 as follows. A layer of a PPV precursor polymer, fabricated according to a sulphonium precursor route ["Precursor route chemistry and electronic properties of poly(p-phenylene vinylene), poly(2,5-dimethyl-p-phenylene vinylene) and poly(2,5-dimethoxy-p-phenylene vinylene)" P. L. Burn, D. D. C. Bradley, R. H. Friend, D. A. Halliday, A. B. Holmes, R. W. Jackson and A. Kraft, *J. Chem. Soc. Perkin Trans. 1*, 1992, 3225-3231], was spin-coated onto a glass plate coated with ITO and thermally converted to PPV. In the other type of bilayer device, a transporting layer of PVK was spin-coated from solution directly onto ITO.

Next, a layer of the polymer poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) 1 was spin-coated onto the PPV layer followed by a layer of aluminium or calcium deposited under

vacuum onto the polymer layer. Contacts were attached and a connection made to a DC power source. Application of a forward bias voltage resulted in emission of yellow-green light with an emission maximum at about 2.3 eV (*ca.* 550 nm), and a brightness in excess of 4,500 cd/m². Internal efficiencies of about 1.5% were observed with calcium as the cathode.

Based on the illustrative examples it is evident that highly efficient devices can be obtained by the dehydrohalogenation route to prepare adjacently substituted arylene vinylene polymers, such as 2,3-disubstituted-1,4-phenylene vinylene polymers from monomers carrying aryl, heteroaryl, alkyl, and branched alkyl substituents linked either by carbon or heteroatom linkages to the aromatic backbone of the polymer.

The adjacent substituents can be selected from H, R, RO-, RS-, and RR'N-, where R=C₅H₁₁, C₆H₁₃, C₇H₁₅ or C₈H₁₇, etc. and branched derivatives thereof, and aryl (Ar) where Ar = aryl or heteroaryl or fused derivatives thereof. Preferable substituents are those which solubilise the final polymer. These include branched alkyl, aralkyl and the corresponding alkoxy derivatives. The most preferred substituent is the butyloxy, and other preferred substituents are ethylhexyl(oxy) and 3',7'-dimethyloctyl (oxy). Other carbon chains such as alkyl or alkoxy substituents carrying up to ten carbon atoms and branching substituents are advantageous. Such substituents could be selected in any combination, and are not limited to those listed.

Circular effects can be achieved with any conjugated polyarylenevinylene polymer or other conjugated polymer (polyfluorene, polythienylene, polynaphthalene, polyphenylene, polypyridine, polyquinoline, polyquinoxaline, poly[thienylene-co-phenylene] etc.) or a copolymer arising from a fluorescent unit carrying a distyrylbenzene fragment with the 2,3-disubstitution at least on the aromatic rings. The preferred polymers arise from poly(arylene vinylene) conjugated units carrying an adjacent disubstitution pattern. Most preferably, 2,3-disubstituted bishalomethylbenzene derivatives serve as starting monomers for the conjugate polymer products.

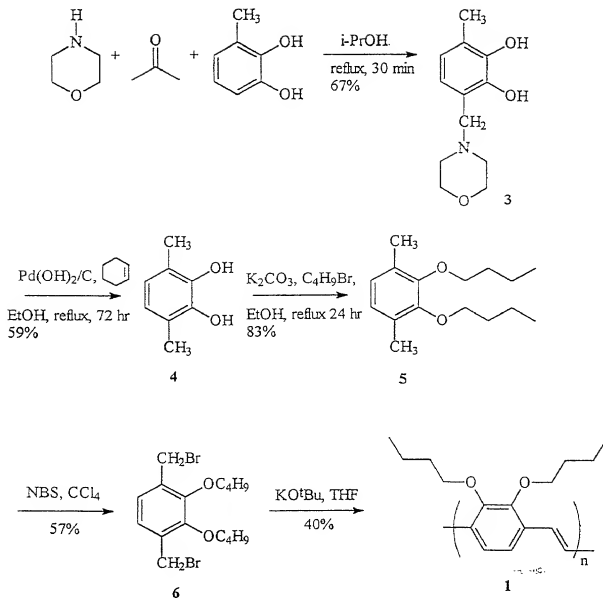
The preferred synthesis involves dehydrohalogenation condensation polymerisation using potassium t-butoxide as a base in various solvents such as tetrahydrofuran or dioxane. The resulting polymer is solution processible and has a good film forming property for polymer

electroluminescent devices. Polymers for 1,4-bis(halomethylbenzene) monomers have been disclosed in US 5,558,904. These afforded insoluble polymers. The adjacent disubstitution in the present invention is achieved owing to the method of synthesis of the polymer, and leads to a product polymer that is solution processible, and having a surprising fluorescence emission wavelength and efficiency.

Previous examples with a 2,3-diphenyl (diaryl) substitution pattern as disclosed in US 5,558,904 would not be expected to demonstrate these features, based on the lack of solubility of the final polymer. This is disclosed in detail in H. Antoniadis *et al.*, *Polym. Adv. Tech.*, 1997, 8, 392. In that case solution processibility required the use of a precursor route to allow processing and generation of the final polymer.

Examples

A method of preparing the conjugated polymer PDB-PPV 1 involves the preparation of the monomer of formula $\text{Br-CH}_2\text{-Ar-CH}_2\text{-Br}$ which is subjected to polymerisation with six equivalents of base (potassium tert-butoxide preferably in THF or dioxane) to give the desired polymer, which is soluble in organic solvents such as chloroform and tetrachloroethane. The synthesis of the polymer is shown in scheme 4 below:



Scheme 4: Preparation of PBD PPV 1

Example 1: Preparation of monomer 6

Methyl catechol derivative 3 was synthesised by performing a Mannich reaction with formaldehyde and morpholine following the method described by Helgeson *et al.* (*J. Am. Chem. Soc.*, 1997, 99, 6411). Transfer hydrogenation using palladium hydroxide on carbon to remove the morpholine group in the presence of a hydrogen donor (Hanessian *et al.*, *Synthesis*, 1981, 118, 396) subsequently produced the dimethyl catechol 4 in reasonable yield (59%). *O*-alkylation was

then carried out using a copious excess of potassium carbonate and dibutyl bromide to give a reasonably high yield (83%) of dialkoxy-xylene 5. Radical bromination of the xylene with a slight excess of *N*-bromosuccinimide in carbon tetrachloride as given in Gruter *et al*, *J. Org. Chem.*, 59, 4473 gave the monomer 6 in comparatively high yield (57%).

Example 2: Preparation of polymer 1

A degassed solution of the monomer 6 (0.24 g, 0.6 mmol) in dry THF (16 cm³) was added slowly over 20 min to a degassed solution of potassium tert-butoxide (0.41 g, 3.6 mmol) in dry THF (16 cm³) at room temperature. The reaction mixture was stirred at room temperature under nitrogen for 18 h, after which it was poured into methanol. The resultant yellow precipitate was collected by filtration and re-precipitated into methanol. The polymer 1 was collected as a bright yellow solid (60 mg, 40%).

Found: C, 76.6; H, 9.1; Br, 0; [C₁₆H₂₂O₂]_n requires C, 78.0; H, 9.0; Br, 0 %

GPC assay in CHCl₃ revealed M_w 2,120,000, M_n 361,000 and M_w/M_n 5.9;

λ_{max} (CHCl₃)/nm 444; λ_{max} (film)/nm 450;

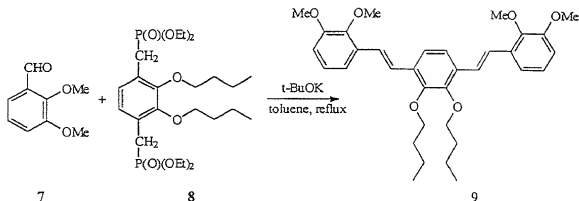
PL emission (max)/nm 551 (2.25 eV); PL efficiency 40 %; EL emission (max)/eV 2.28.

Example 3: Fabrication of a 2-layer LED with polymer 1

A film of PPV (ca. 100 nm in thickness) was prepared by spin-coating a solution of a sulphonium precursor polymer onto a glass plate coated with indium tin oxide and thermally converting the film at 230°C in vacuum for 6h. A 1% (w/v) solution of the polymer 1 in chloroform was spin-coated on top of the converted PPV film to give a uniform film of about 100 nm thick. The structures were placed on top of a mask, permitting the deposition of aluminium or calcium on the coated film surface inside a metal evaporator. Metal layers were of typically 500-1000 Å in thickness. Metal contacts were then attached to the electrodes and connected to a DC source. The active device area was typically 4 mm².

The bilayer device (ITO/PPV/PDB-PPV/Ca) shows maximum efficiency 1.5 % with luminance in excess of 4,500 cd/m² with turn-on voltage at 9V. A bilayer device was also constructed with PVK as the hole-transporting layer produced a maximum efficiency of 0.6% with Al cathodes.

Example 4: Preparation of the model oligomer 9



Scheme 5: Preparation of dialkoxy-substituted oligomer 9

9 is obtained as pale green crystals, m.p. 80-81; λ_{max} (CHCl_3) 362 nm, (film) 366 nm; blue-green fluorescence, PL_{max} (film) 2.6 eV

A mixture of the 2,3-dimethoxybenzaldehyde 7 (0.33 g, 2.0 mmol) and 1,4-[(2,3-dibutoxyxylylene)-bis(diethylphosphonate) 8 (0.52 g, 1.0 mmol) in toluene (10 cm^3) was stirred and heated to ca. 100°C under an atmosphere of nitrogen. Potassium tert-butoxide (0.35 g, 3.0 mmol) was added all at once into the hot mixture resulting in a colour change to orange-brown. The mixture was then heated to reflux for 4 h. After allowing to cool to room temperature, toluene was added (20 cm^3) followed by hydrolysis with acetic acid (10% aq., 20 cm^3). The organic layer was separated, washed with water until the organic layer tested neutral. The organic fraction was dried, followed by removal of the solvent under reduced pressure to yield a yellow oil. The product 9 was isolated by column chromatography (9:1 hexane:diethyl ether v/v) and further purified by recrystallisation from methanol to give greenish-white needles (0.35 g, 64%).

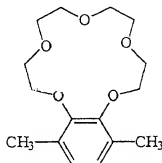
M.p. 80.0-81.0°C;

δ_{H} (250 MHz, CDCl_3) 7.49-7.47 (6H, m, Ar-H & CH=CH), 7.30-7.26 (2H, m, ArH_a), 7.08 (2H, t, J 8.0, ArH_b), 6.86-6.83 (2H, m, ArH_c), 4.04 (4H, t, J 6.6, ArOCH₂), 3.89-3.87 (12H, m, ArOCH₃), 1.88-1.77 (4H, m, CH₂), 1.64-1.49 (4H, m, CH₂), 1.00 (6H, t, J 7.2, CH₃);

δ_c (63.5 MHz; CDCl_3) 153.1 (C, Ar), 150.6 (C, Ar), 147.1 (C, Ar), 132.0 (C, Ar), 131.7 (C, Ar), 124.2 (CH, Ar), 124.1 (CH, Ar), 123.4 (CH, Ar), 121.0 (CH, Ar), 117.9 (CH, Ar), 111.3 (CH, Ar), 73.7 (OCH_2), 61.1 (OCH_2), 55.8 (OCH_2), 32.4 (CH_2), 19.4 (CH_2), 14.0 (CH_3);
 m/z (CI) 547 (MH^+ , 75%), 402 (10), 166 (40), 72 ($\text{C}_6\text{H}_8\text{O}$, 60), 52 (C_4H_4 , 70);
 Found (MH^+) 547.3060; $\text{C}_{34}\text{H}_{42}\text{O}_6$ requires 546.2981;
 Found: C, 74.7; H, 7.8; $\text{C}_{34}\text{H}_{42}\text{O}_6$ requires C, 74.7; H, 7.8 %;
 λ_{max} (CHCl_3/nm) 366; λ_{max} (film/nm) 362;
 PL_{max} (film/nm) 477; PL efficiency (solid state) *ca.* 80%.

The X-ray structure of the oligomer 9 (see Figure 1) shows an unusual cisoid-like conformation around the *trans*-vinylene bond. The benzene rings are twisted out of the plane of the vinylene linkage by about 15° and the benzene rings in turn are twisted at a 30° angle from one another in a regular pattern. This twist will eventually cause an interruption in the polymer backbone conjugation after every 4 benzene rings. The oligomer shows high PL efficiency (*ca.* $8 \pm 8\%$) in the solid state.

Synthesis of Monomers



14

3,6-Dimethylbenzo-15-crown-5, 14

To a solution of dimethyl catechol 4 (2.5 g, 18 mmol) in tetrahydrofuran (110 cm^3) under a nitrogen atmosphere was added sodium hydroxide (1.44 g, 36 mmol). The mixture was left stirring for a hour, and a solution of tetraethyleneglycol-di-*p*-tosylate (9.05 g, 18 mmol) in tetrahydrofuran (50 cm^3) was added in dropwise over 30 min. The mixture was refluxed for 22 h. The mixture was cooled, the solvent removed and the residue taken up in dichloromethane

(200 cm³). The organic layer was extracted with water (3 x 100 cm³) and dried over MgSO₄. The solvent was removed under reduced pressure to yield a brown crude. The benzo crown ether was isolated by flash column chromatography (hexane followed by 9:1 hexane:ethyl acetate v/v) to yield the ether 14 as a colourless oil (2.2 g, 41%). R_f 0.25 (6:4 hexane:ethyl acetate v/v);

ν_{\max} (KBr)/cm⁻¹ 2860, 1580, (Ar), 1281, 1134, 1081 (C-O);

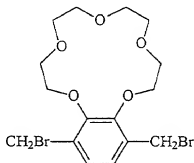
δ_{H} (400 MHz; CDCl₃) 6.79 (2H, s, Ar-H), 4.11 (2 x 2H, t, J 5.2, Ar-OCH₂), 3.96 (2 x 2H, t, J 5.2, ArO-CH₂CH₂), 3.74 (4 x 2H, m, OCH₂), 2.22 (6H, s, ArCH₃);

δ_{C} (400 MHz; CDCl₃) 150.6 (C, Ar), 150.6 (C, Ar), 129.8 (C, Ar), 129.8 (C, Ar), 125.4 (CH, Ar), 125.4 (CH, Ar), 71.9 (CH₂), 71.9 (CH₂), 71.1 (CH₂), 71.1 (CH₂), 70.6 (CH₂), 70.6 (CH₂), 70.3 (CH₂), 70.3 (CH₂), 15.8 (CH₃), 15.8 (CH₃);

m/z (CI) 297 (MH⁺, 20%), 244 (5), 164 (10);

Found (MH⁺) 297.1702; C₁₆H₂₄O₅ requires 296.1624;

Found: C, 64.4; H, 8.1; C₁₆H₂₄O₅ requires C, 64.8; H, 8.2 %



10

3,6-Bis (bromomethyl)-benzo-15-crown-5, 10

A mixture of the benzo-crown ether 14 (1.77 g, 5.97 mmol), *N*-bromosuccinimide (2.18 g, 12.2 mmol) and benzoyl peroxide (0.14 g, 0.6 mmol) in carbon tetrachloride (50 cm³) was heated to reflux for 5 h after which the succinimide had floated to the surface of the solvent mixture. After allowing to cool to room temperature, the mixture was filtered through Celite® and washed with ether. The filtrate was collected and the solvent removed under reduced pressure. The residue was taken up in ether (100 cm³) and the organic layer extracted with water (2 x 50 cm³). The organic fraction was dried over MgSO₄ and the solvent removed under reduced pressure to

produce the crude product as an orange-coloured solid. Recrystallisation from boiling hexane yielded the bis bromomethyl product 10 as a colourless solid 10 (0.56 g, 21 %). M.p. 127.5-128.5°C; R_f 0.32 (6:4 hexane:ethyl acetate v/v);

ν_{\max} (neat)/ cm^{-1} 2875, 1451 (Ar), 1287, 1146, 1057 (C-O), 677 (C-Br);

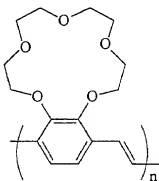
δ_H (250 MHz; CDCl_3) 7.09 (2H, s, Ar-H), 4.53 (4H, s, CH_2Br), 4.33 (4H, t, J 5.0, ArOCH_2), 4.00 (4H, t, J 5.0, $\text{ArOCH}_2\text{CH}_2$), 3.75 (8H, m, OCH_2);

δ_C (100 MHz; CDCl_3) 150.9 (C, Ar), 150.9 (C, Ar), 133.4 (C, Ar), 133.4 (C, Ar), 126.1 (CH, Ar), 126.1 (CH, Ar), 72.6 (CH_2), 72.6 (CH_2), 71.1 (CH_2), 71.1 (CH_2), 70.4 (CH_2), 70.4 (CH_2), 27.7 (CH_2), 27.7 (CH_2);

m/z (CI) 470 ($\text{M}+\text{NH}_4^+$, 58 %), 390 (5), 312 (12), 44 (15);

Found ($\text{M}+\text{NH}_4^+$) 470.0178; $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Br}_2$ requires 451.9835;

Found: C, 42.5; H, 4.8; Br, 35.2; $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Br}_2$ requires C, 42.5; H, 4.9, Br 34.9 %



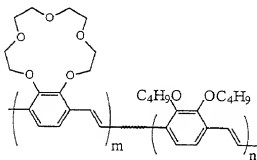
2

15C5-PPV, 2

A degassed solution of KO^tBu (0.1 g, 0.88 mmol) in dry THF (16 cm^3) was added slowly over 20 min to a degassed solution of the dibromide monomer 10 (0.2 g, 0.44 mmol) in dry THF (16 cm^3) at room temperature. The reaction mixture was stirred at ambient temperature under nitrogen for 18 h, after which it was poured into methanol (600 cm^3) with stirring. The resultant yellow precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum CHCl_3 and re-precipitated into methanol (600 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer 9 as an orange solid (75 mg, 58 %).

ν_{\max} (film)/ cm^{-1} 2925, 2867, 1492 (Ar), 1285, 1133 (C-O), 938 (trans-vinylene);
 δ_{H} (400 MHz; CDCl_3) 7.50-7.25 (2H, br m, conjugated unit), 4.25 (4H, br m, ArOCH_2), 4.05 (4H, br m, $\text{ArOCH}_2\text{CH}_2$) 3.80 (8H, br m, OCH_2);
 δ_{C} (100 MHz; CDCl_3) 150.5, 131.5, 121.0 (C, conjugated aromatic carbons), 71.5, 70.5, 70.5 (crown ether CH_2) (conjugated units not visible using 8,000 scans);
 Found: C, 62.6; H, 6.8; Br, 1.4; $[\text{C}_{16}\text{H}_{20}\text{O}_5]_n$ requires C, 65.7; H, 6.9; Br, 0 %.
 GPC assay in CHCl_3 revealed M_w 10.7×10^6 , M_n 126×10^3 and M_w/M_n 84;
 λ_{\max} (film)/nm 442.

Synthesis of Copolymers



12

15C5-DB PPV copolymer, 12

A degassed solution of KO^tBu (0.26 g, 2.2 mmol) in dry THF (40 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, bis(bromomethyl)-benzo-15-crown-5 monomer 10 (0.2 g, 0.44 mmol) and 2,3-dibutoxy-1,4-bis(bromomethyl) benzene 6 (0.18 g, 0.44 mmol) in dry THF (40 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 6 h, and poured into methanol (500 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum CHCl_3 and re-precipitated into methanol (500 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a bright orange solid (0.15 g, 35 %).

ν_{\max} (film)/ cm^{-1} 2956, 2869, 1436 (Ar), 1283, 1135 (C-O), 974 (trans-vinylene);

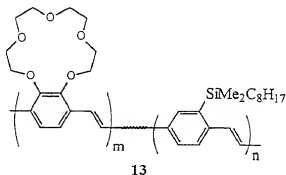
δ_H (400MHz; $CDCl_3$) 7.49-7.45 (H-conjugated units), 4.22-3.73 (2OH, m, br, OCH_2 & $ArOCH_2$), 1.84-1.57 (8H, m, br, CH_2), 1.03-0.99 (6H, m, br, CH_3);

m:n ratio determined by 1H NMR to be approximately 1:1;

Found C, 70.0; H, 7.8; Br, 0.9; $[C_{32}H_{42}O_7]_n$ requires C, 71.4; H, 7.8; Br, 0%;

GPC assay in $CHCl_3$ revealed M_w 2.7×10^6 M_n 24×10^3 and M_w/M_n 110;

λ_{max} ($CHCl_3$)/nm 442; λ_{max} (film)/nm 452.



15C5-DMOS PPV copolymer, 13

A degassed solution of KO^tBu (0.16 g, 1.3 mmol) in dry THF (12 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, 10 (0.14 g, 0.3 mmol) and 2-methyloctylsilyl-1,4-bis(bromomethyl) benzene 11 (0.13 g, 0.3 mmol) in dry THF (13 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 8 h, after which it was poured into methanol (200 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum $CHCl_3$ and re-precipitated into methanol (200 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a light orange solid (0.13g, 76%).

ν_{max} (film)/ cm^{-1} 2923, 2856, 1459 (Ar), 1283, 1137 (C-O), 937 (trans-vinylene);

δ_H (400 MHz; $CDCl_3$) 7.67-6.95 (9H, m, br, H-conjugated unit), 4.22 (4H, s, br, $ArOCH_2$), 4.05 (4H, s, br, $ArOCH_2CH_2$), 3.79 (8H, s, br, OCH_2), 1.31-1.22 (12H, m, br, CH_2), 0.88 (5H, m, br, CH_2CH_3), 0.43-0.36 (6H, m, br, CH_3); m:n ratio determined by 1H NMR to be approximately 1:1;

Found C, 71.4; H, 8.3; Br, 1.9; $[C_{34}H_{48}O_5Si]_n$ requires C, 72.3; H, 8.6; Br, 0%;

GPC assay in $CHCl_3$ revealed M_w 286×10^3 M_n 37×10^3 and M_w/M_n 7.7;

λ_{max} (CHCl₃)/nm 434; λ_{max} (film)/nm 442.

The PL efficiency and the EL efficiency of the copolymers 12 and 13 and the corresponding efficiencies of DMOS-PPV and 1 are shown in Table 1 below. In particular, the electroluminescence efficiency of 12 and 13 is high, whilst these copolymers still have good photoluminescence efficiencies.

Table 1: Summary of efficiency data for the polymers 12 and 13 in comparison with DMOS-PPV and DB-PPV 1.

Polymer	PL efficiency ^a (%)	EL internal quantum efficiency ^b (Cd/A)
15C5-DB PPV 12	38	0.35
15C5-DMOS PPV 13	48	0.3
DMOS-PPV	60	not available
DB-PPV 1	40	0.015

^ameasurements made on films

^bmeasurements made on ITO/polymer/Al devices, thickness 100-200 nm.

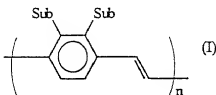
References

- US 3,401,152, Wessling *et al.*
- US 5,558,904, Hsieh *et al.*
- US 5,189,136, Wudl, F.
- J. H. Burroughes *et al.*, *Nature*, 1990, 365, 47.
- H.G. Gilch *et al.*, *J. Poly. Sci. 1-A*, 1966, 4, 1337.
- B. R. Hsieh *et al.*, *Adv. Mater.*, 1995, 7, 36.
- WO 95/32526, Staring & Demandt
- H. Antoniadis *et al.*, *Poly. Adv. Tech.*, 1997, 8, 392

Claims:

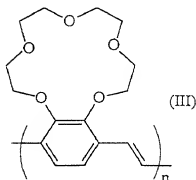
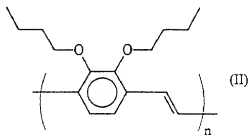
1. A conjugated poly(1,4-arylene vinylene) compound comprising an arylene unit having adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.
2. A compound according to claim 1, wherein the substituents are independently selected from:
 - (i) R-, RO-, RS-, and RR'N-
wherein R and R' are independently: a straight or branched chain alkyl group, alkenyl group, or alkynyl group having 1-10 carbon atoms; an aryl group; or an aromatic or non-aromatic heterocyclic group; and
 - (ii) a group in which the adjacent substituents together form a cyclic group, the cyclic group containing, in addition to the two carbon atoms of the arylene unit to which it is attached, 1-10 carbon atoms and 0 or 1-6 hetero atoms selected from O, S and N.
3. A compound according to claim 2, wherein the cyclic group contains 2-6 hetero atoms.
4. A compound according to any preceding claim, wherein one or both of the adjacent substituents are independently selected from a branched alkyl group and a branched alkoxy group.
5. A compound according to any preceding claim, wherein each of the carbon atoms at the adjacent substituted positions of the aryl unit is attached to its substituent via a hetero atom, selected from O, S or N.
6. A compound according to any preceding claim, wherein the substituents are solubilising substituents.

7. A compound according to any preceding claim, wherein one or both of the adjacent substituents are independently selected from butyloxy, ethylhexyloxy and 3',7'-dimethyloctyloxy groups.
8. A compound according to any preceding claim, wherein the arylene unit is a fluorene unit, a phenyl unit, a thienyl unit, a naphthalene unit, a pyridine unit, a quinoline unit, a quinoxaline unit, or a unit comprising a thienylene and a phenylene.
9. A compound according to any preceding claim, wherein the poly(arylene vinylene) is a copolymer comprising a fluorescent unit carrying a distyryl-2,3-substituted-benzene fragment.
10. A compound according to any preceding claim, which is a poly(phenylene vinylene) compound.
11. A compound according to claim 10, wherein the adjacent substituents are in the 2-position and the 3-position of the phenylene residue.
12. A compound according to claim 11, of formula (I):



wherein Sub is a substituent as defined in any of claims 1-7, the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the formula in the polymer.

13. A compound according to claim 11, of formula (II) or formula (III):



wherein the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the respective formula in the polymer.

14. A method for the production of a compound as defined in any preceding claim, which method comprises polymerising a bis(halomethyl) substituted aryl monomer in the presence of a base to form a poly(arylene vinylene), wherein the aryl monomer has adjacent substituents on the aryl residue.
15. A method according to claim 14, wherein the monomer is a bis(chloromethyl), bis(bromomethyl) or bis(iodomethyl) monomer.
16. A method according to claim 14 or claim 15, wherein the base is potassium tertiary butoxide.
17. A component or device comprising a compound as defined in any of claims 1-13.

18. A component or device according to claim 17, which is an electric, electronic, optical or optoelectronic component or device.
19. A component or device according to claim 17 or claim 18, which is a photoluminescent or electroluminescent component or device.
20. A light emitting diode comprising a component or device as defined in any of claims 17-19.
21. A method for producing a component or device as defined in any of claims 17-20, which method comprises coating a solution of a compound as defined in any of claims 1-13 onto a substrate to form a film.
22. A method according to claim 21, wherein the substrate is ITO.
23. A method according to claim 21 or claim 22, wherein the solution is a chloroform solution.
24. A method according to any of claims 21-23, wherein the solution is spin-coated onto the substrate.
25. Use of a light emitting diode as defined in claim 20, in an electric, electronic, optical or optoelectronic component or device.
26. Use of a poly(arylene vinylene) compound comprising an arylene unit having adjacent substituents, in an electric, electronic, optical or optoelectronic component or device for producing blue-shifted electroluminescence or photoluminescence in said device.
27. Use according to claim 26, wherein the adjacent substituents are as defined in any of claims 1-7.

28. Use according to claim 26 or claim 27, wherein the arylene unit is as defined in any of claims 8-13.
29. Use according to any of claims 26-28, wherein the electric, electronic, optical or optoelectronic component or device is a light emitting device, such as a light emitting diode.

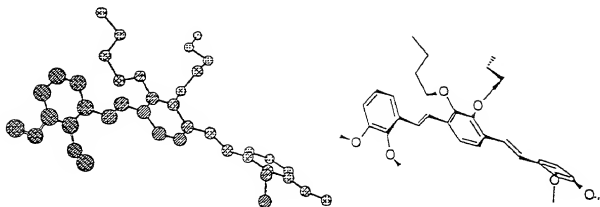


FIGURE 1

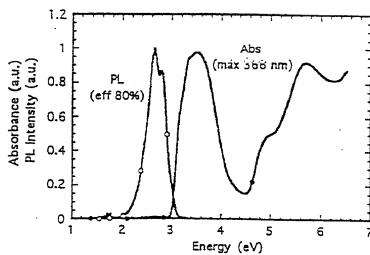


FIGURE 2

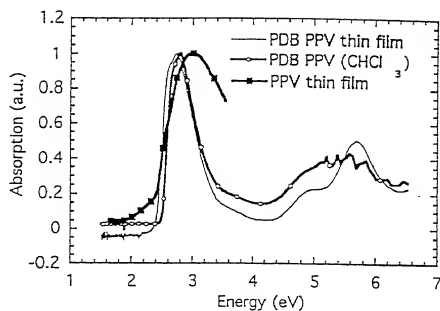


FIGURE 3

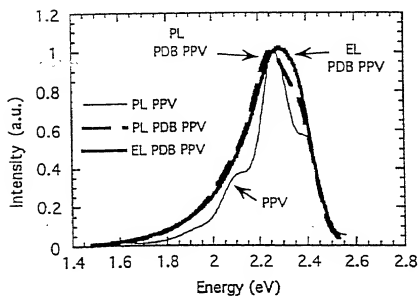


FIGURE 4

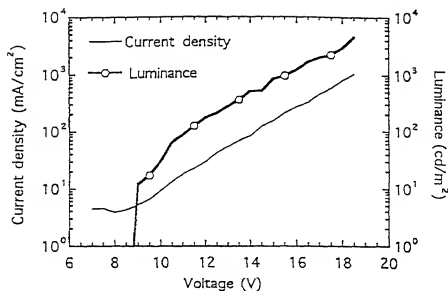


FIGURE 5

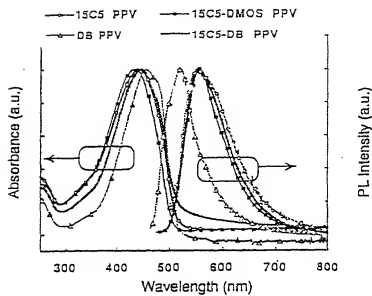


FIGURE 6

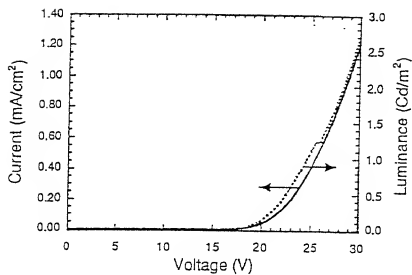


FIGURE 7

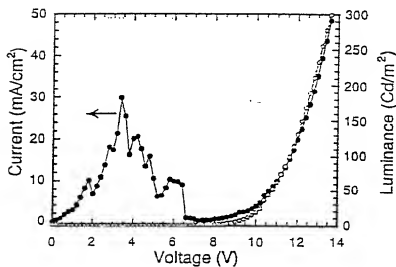


FIGURE 8

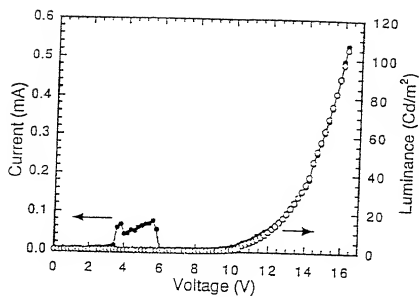


FIGURE 9

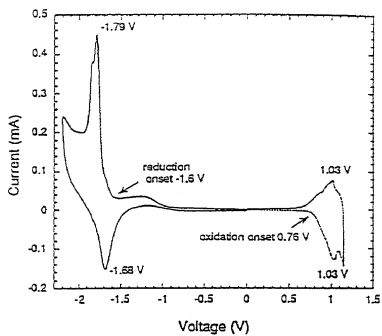


FIGURE 10

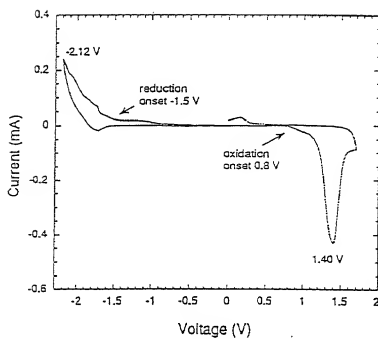


FIGURE 11

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

POLYMERIC MATERIALS FOR ELECTROLUMINESCENT DEVICES

the specification of which was filed in the U.S. Patent Office on April 20, 2000 under U.S. Serial No. 09/529,873.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign PCT Application(s) and any priority claims under 35 U.S.C. §119:	Priority Claimed
PCT/GB98/03154 (Number) PCT (Country if PCT so indicate) 21 October 1998 (DD/MM/YY Filed)	[X] [] YES NO
GB9814815.8 (Number) Great Britain 08 July 1998 (Country) (DD/MM/YY Filed)	[X] [] YES NO
GB9722102.2 (Number) Great Britain 21 October 1997 (Country) (DD/MM/YY Filed)	[X] [] YES NO

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(filing date)	(status-patented, pending, abandoned)
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(Application Serial No.)	(filing date)	(status-patented, pending, abandoned)
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PCT Applications designating the United States:

(PCT Appl. No.)	(U.S. Ser. No.)	(PCT filing date)	(status-patented, pending, abandoned)
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I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

2

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

X Andrew B Holmes

X 26 June 2000 X

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Date

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Date

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Full name of second or joint inventor: Steven Carl Moratti

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I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Inventor's signature

Date

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